Theoretical investigations of anisotropic optical properties of distorted 1T ReS₂ and ReSe₂ mono-, bi-layers and in the bulk limit

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Abstract

We present a theoretical study of electronic and optical properties of the layered ReX₂ compounds (X = S, Se) upon dimensional reduction. The effect on the band gap character due to interlayer coupling is studied by means of self-energy corrected *GW* method for optimized and experimental sets of structure's data. Induced changes on the optical properties as well as optical anisotropy are studied through optical spectra as obtained by solving the Bethe-Salpeter equation. At the G_0W_0 level of theory, when decreasing the thickness of the ReS₂ sample from bulk to bilayer and to a freestanding monolayer the band gap remains direct, despite a change of the band-gap nature, with values increasing from 1.6, 2.0 and 2.4 eV respectively. For ReSe₂, the fundamental band gap changes from direct for bulk phase (1.38 eV) to indirect in bilayer (1.73 eV) and becomes again direct for a single layer (2.05 eV). We discuss these results in terms of the renormalization of the band structure. We produce the polarization angular dependent optical response to explore the optical anisotropy present in our results, as well as the fine structure of the lowest excitonic peaks present in absorption spectra.

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I. INTRODUCTION

Isolation of a single and few layers from bulk's systems in many Transition Metal Dichalcogenides (TMDCs) has renewed the interest on their structural and optical properties broadly studied in bulk¹⁻⁶. Dimensionality reduction's effects have motivated recent works on monolayers (MLs) and few layer's thickness systems, since it has been shown for the first time in MoS₂ that, upon dimensional confinement, the indirect band gap in bulk become direct in a ML^{7,8}. Today, several others systems like W-based systems have shown similar behavior⁹⁻¹¹.

Such is the case of ReX₂ (X = S, Se) compounds, layered crystals belonging to TMDCs semiconductor's family which crystallize in a distorted 1T diamond-chain structure with triclinic symmetry unit cell usually denoted 1T'. The successful isolation of a single and few layers of ReX₂, has allowed their structural and optical characterization¹²⁻¹⁵. However, there are many aspects on ReX₂ optoelectronic properties still remain to be clarified. See Ref.[16] for a recent review on experimental aspects of these TMDCs.

Based on their findings, some groups, have argued that in ReS₂ the interlayer coupling is negligible and the stacked layers in bulk behave as electronically and vibronically decoupled monolayers^{12,17}. In contrast, recent Photo-Luminescence (PL) and Reflectance spectroscopy measures in bulk and few layer thickness samples of ReS₂ reveal a dependence of the optical properties on the thickness¹⁵. Additionally, it was usually claimed that ReS₂ shows a transition from indirect to direct optical band gap when the dimensionality is reduced from bulk to ML as in many other TMDCs¹⁸. This is in contradiction with the work of Tongay *et al.* who have reported an unchanged indirect band gap from bulk to ML. A very recent work on ReS₂ bulk, using gated field-effect transistors, tends to confirm the indirect character of the gap¹⁹, when recent ARPES experiments tends to prove the contrary²⁰.

From the theoretical side, some attempts to clarify these subjects using different methodologies can be found in the literature. Early results on bulk's band-structures based on Density Functional Theory (DFT) have shown ReX₂ compounds to be indirect band gap semiconductors²¹, while more recent theoretical studies tend to prove the contrary¹². For ML and few-layers systems at standard DFT level, meaning that many-body screening effects are scarcely described, the fundamental gap is found to be direct but largely underestimated for ReS₂^{12,22-24}. On contrary, a ReSe₂ ML has an indirect band gap when explicit electron-electron screening is taken into account^{14,22}. The only attempts of describing ReX₂ ML with

the use of GW self-energy correction also give a direct gap of 2.38 eV at Γ -point, i.e at the center of the first Brillouin Zone (BZ), for ReS_2 as for ReSe_2 ML^{22,25}. However for the latter case nothing is said about the difference between the indirect and the direct transition, since it is known that for different computational settings and/or a small strain effect, it is easy to influence the position of valence band maxima and conduction band minima²⁶.

The presence of a strong optical anisotropy in ReX_2 compounds^{27–30}, unlike Mo or W based hexagonal TMDCs, is due to their particular crystalline structure (see Fig. 1). It is believed that the structural distortion leads to a much weaker interlayer coupling, so the band renormalization is supposedly absent and so bulk ReX_2 should behave as decoupled monolayers^{12,13}. However Aslan *et al.*¹⁵, demonstrated that the anisotropic optical properties of single- and few-layer ReS_2 crystals are different through polarization-resolved reflectance and photoluminescence spectroscopy. They have found that the near band-edge excitons in ultra-thin crystals absorb and emit light with preferred linear polarizations. Likewise, they have observed that the transition energies of the excitons can be tuned with layer thickness. They have thus established that ultra-thin ReS_2 has optical transitions with strengths and transition energies that depend on thickness and polarization of the optical radiation.

Here we propose to explore theoretically the optical properties of freestanding ML, bilayers (BL) of ReX_2 systems by including excitonic effects through GW and Bethe-Salpeter Equation (BSE) type calculations and compare them to bulk's spectra. We address the question about the character of the fundamental band gap upon dimensional reduction and we discuss it in terms of screening effects due to the presence of neighboring layers. Likewise, we discuss the dependence of the optical spectra on the thickness and on the polarization angle by rotating the dielectric tensor's components on the layer's plane. The present paper is organized as follows: in the section II we present the computational details for ML, BL and bulk calculations. In the section III the results concerning quasi-particle band-structure of ML, BL and bulk as well as the effects on the nature of the transition band-gaps when increasing the thickness are presented. Optical adsorption spectra for ML, BL and bulk are discussed in Section IV. Finally, we present main conclusions of this work.

II. COMPUTATIONAL DETAILS AND ATOMIC STRUCTURES

The atomic structures, the quasi-particle band structures and optical spectra are obtained from DFT calculations using the VASP package^{31,32}. Perdew-Burke-Ernzerhof (PBE) functional³³ is used as approximation of the exchange-correlation electronic term. Core electrons are treated by the projector augmented wave scheme^{34,35}. Fifteen electrons for Re atoms and six for S, Se ones are explicitly included in valence states. All atoms are allowed to relax with a force convergence criterion below 0.005 eV/Å. During bulk and BL geometry optimization calculations, the functional of Langreth and Lundqvist^{36,37} is used in the vdW-DF2 form^{38,39} in order to describe accurately long-range correlations between layers. A grid of $6 \times 6 \times 1$ k-points has been used, in conjunction with a vacuum height of around 20 Å, to take benefit of error's cancellation in the band gap estimates⁴⁰, and to provide the imaginary part of the dielectric constant, a key quantity in absorption spectra in reasonable agreement with experiments as suggested in different works^{41,42} for ML and BL calculations. A grid of $6 \times 6 \times 6$ k-points has been used for bulk calculations. As it can be seen in Appendix A by using a $6 \times 6 \times 1$ grid, it ensures a variation of only 50 meV compared to a $12 \times 12 \times 1$ calculation for the position of the first excitonic peak. We use an energy cutoff of 400 eV and a gaussian smearing with a width of 0.05 eV is used for partial occupancies, when a tight electronic minimization tolerance of 10^{-8} eV is set to determine with a good precision the corresponding derivative of the orbitals with respect to k needed in quasi-particle band structure calculations. Spin-orbit coupling was also included non-self-consistently to determine eigenvalues and wave functions as input for the full-frequency-dependent GW calculations⁴³ performed at the G_0W_0 level but also at GW_0 level with 2 iterations of the G term, for testing purpose. The total number of states included in the GW procedure is set to 600, in conjunction with an energy cutoff of 100 eV for the response function, after a careful check of the direct band gap convergence, to be smaller than 0.1 eV in function of k-points sampling too. Band structures have been obtained after a Wannier interpolation procedure performed by the WANNIER90 program⁴⁴. Only direct optical excitonic transitions are calculated by solving the BSE^{45,46}, with the inclusion of 6 valence and 8 conduction bands in the diagonalization process for ML and bulk calculations. For the BL systems we use 12 valence and 16 conduction bands with for all optical spectra a broadening parameter of 25 meV is set. From these calculations, we report absorbance values defined as proposed

in Ref. [47], by using the imaginary part of the complex dielectric function $\epsilon_2(\omega)$, with the following formula:

$$A(\omega) = \frac{\omega}{c} \epsilon_2(\omega) \Delta z \quad (1)$$

, where Δz is the vacuum distance between periodic images of ML and BL. This quantity is measurable and supposedly should not depend on the size of calculation cells in the ML/BL perpendicular direction. As pointed out by Bernardi *et al*⁴⁸, Eq. (1) is a Taylor expansion for $\Delta z \rightarrow 0$ of the absorbance defined as $A = 1 - e^{-\alpha_2 \Delta z}$ for a single or bi-layer of a bulk material with a thickness Δz , presenting an absorption coefficient $\alpha_2(\omega) = \frac{\omega \epsilon_2(\omega)}{c n(\omega)}$, where for this case the refractive index is $n = 1$, since the considered ML/BL is surrounded by vacuum only.

Considering the lattice parameters and atomic positions in the bulk, as well as in ML or BL stacking, few issues need to be addressed. In the bulk's case, as it can be seen in Table I, the lattice parameters and the angles obtained upon geometry optimization using a van der Waals correction are in good agreement with experimental data for both materials. We recall that the $1T'$ structure observed experimentally for bulk ReX_2 phases and used here for atomic configurations is triclinic, the corresponding space group being $P\bar{1}$. As a consequence, MLs and bulk present a center of inversion, the symmetry point group is thus C_i . For the ML systems, PBE optimization results (denoted D_1) are in line with previous theoretical studies^{14,22,49}. Additionally we also report the D_2 structure as proposed in Ref. [50], which corresponds to a diamond-flip, or a displacement of Re atoms along the lattice vector b , with a small strain. Interestingly it implies a slight decrease of around 1% of the a parameter. Since the work of Tongay *et al.*¹², it is believed that contrarily to others TMDCs, ReX_2 systems possess very weak interlayer interactions. However when non-local correlation are properly taken into account it appears that the binding energy between two layers in the simplest AA-stacking (a simple superposition of the two layers), is roughly the same as in the emblematic MoS_2 case, see Appendix B.

In order to investigate the BL stacking, we have kept fixed the lattice parameters from ML D_1 structures and displaced the upper layer in different direction, along $\vec{a}$, along $\vec{b}$ and perpendicular to $\vec{b}$, as proposed in previous studies^{12,49}. We have taken into account the effects of van der Waals forces in the exchange-correlation term contrarily to previous works, and thus the resulting optimized stacking order is slightly different. For both ReS_2 and ReSe_2 systems the most stable stacking are yielded when the second layer is displaced

TABLE I. Calculated and experimental lattice parameters and angles for bulk and monolayer ReX_2 systems.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
ReS₂						
Exp Bulk ^a	6.510	6.417	6.461	106.47	88.38	121.10
DFT Bulk	6.57	6.42	6.34	104.2	93.7	119.8
ML D ₁	6.57	6.40	-	-	-	119.8
ML D ₂	6.50	6.40	-	-	-	118.7
ReSe₂						
Exp Bulk ^b	6.716	6.602	6.728	104.90	91.82	118.94
DFT Bulk	6.86	6.68	6.76	103.8	95.0	119.8
ML D ₁	6.84	6.65	-	-	-	119.7

^a Ref. [51]

^b Ref. [52]

by $0.375 \vec{a}$ from the AA-stacking, loosing the presence of a center of inversion in the calculation's cell.. Mind the energy landscape is very flat with minima only separated by energy differences around few tenth of meV, as shown in Appendix C.

III. BAND STRUCTURES AND QUASIPARTICLE BAND-GAPS

A. Monolayer

The G_0W_0 band structures of distorted $1T$ -ReS₂ ML in D₁ and D₂ phases are plotted in Figure 2 along high symmetry directions of the first BZ. A relatively flat dispersion of the bands near Fermi energy is observed, due to the strongly localized characters of the involved orbitals of the Re atoms. Indeed main orbital contributions, estimated by a crude decomposition of the electronic states on atomic spherical harmonics, to the Highest Valence Band (HVB) in Gamma come from the all five 5- d Re orbitals, with a very modest mixing with the 3 p S orbitals, mainly the p_z ones. We recall that in the C_i symmetry point group

FIG. 1. a) Top view and b) side view of distorted 1T monolayer ReX_2 , Re atoms are in grey, X (S, Se) atoms are in yellow. The cell used during calculations is depicted by black line in a). The Re chain is along the $\vec{b}$ direction. c) First Brillouin zone of the ReX_2 monolayer and bulk. For sake of comparison, the notation is the same as the one used in Ref. [25]

the d orbitals are of even parity. For the Lowest Conduction Bands (LCB), the electronic states are mainly distributed on the Re d_{xy} , and d_{z^2} orbitals, with a much stronger mixing with p_x and p_y orbitals of sulfur atoms. This hybridization is thus responsible for the change of parity required to allow the transition. Comparing with others TMDCs like Mo or WX_2 , ReX_2 does not present spin splitting due to Spin-Orbit Coupling (SOC) in the ML limit, since inversion symmetry is present. This has visible effects on its optoelectronic properties as discussed below. Thus HVB and LCB are spin-folded with a negligible splitting between them. Interestingly, band structures of both D_1 and D_2 phases are very similar, with only slight changes of the band curvatures in the K_1 , K_4 valleys for both HVB and LCB. From this result we can extract a value of the fundamental gap located in the center of the first

BZ, E_g^Γ , for ReS₂ ML to be 2.38 eV, in remarkably good agreement with the previous work of Zhong *et al.*²² Mind that when reducing lattice parameters to the experimental values, ReS₂ ML remains direct with a slightly smaller gap, 2.23 eV.

FIG. 2. On the left, the G_0W_0 band structures of ReS₂ monolayer in D₁ (in red) and D₂ (in black) phases. On the right, the G_0W_0 band structures of ReSe₂ monolayer in D₁ phase. The inset presents a zoom around the Γ -point for two set of lattice parameters: the DFT-optimized lattice parameters of D₁ phase and the experimental ones. The energy level of the valence band maximum (in Γ) is set to zero.

The ReSe₂ ML's band structure, with D₁ DFT-optimized lattice parameters, is shown in Figure 2 (right-side). Flat bands near Fermi level are also obtained, making ReSe₂ ML band structure very similar to ReS₂. The fundamental gap remains direct with a value of 2.05 eV. This result is in line with the reported value of 2.09 eV in Ref. [22], but much smaller than the 2.44 eV proposed in the work of Arora *et al.*²⁵ For sake of comparison we report in Figure 2, the behavior of the HVB and LCB around Γ point for the D₁ DFT-optimized lattice parameters and the experimental ones, taken as in the bulk phase. Interestingly when decreasing the lattice parameters, the ReSe₂ fundamental gap becomes indirect, since a maximum (denoted Λ in the HVB along the Γ -K₁ ($-K_4$) direction) pops up, the direct gap remaining 10 meV larger. This observation has been already reported in a previous study of ReX₂ but without any explanation²². The importance of lattice parameters choices have been pointing out in a previous work on MoX₂ ML systems²⁶, especially when Se atoms are involved. As usual, the use of partially self-consistent G_2W_0 calculations, provides larger

band-gaps values, without changing the positions of the VB maxima and CB minima. The direct gap in Γ values are 2.60 eV and 2.23 eV for ReS_2 and ReSe_2 respectively at this level of theory.

B. Bilayer

Figure 3 provides band structures for both ReS_2 and ReSe_2 BLs. In both cases, no spin-splitting is observed. The interlayer coupling impacts the band structure by renormalizing the band gap by roughly 16%. For ReS_2 BL the positions of the CB minimum and the VB maximum remain the same as in the ML case. As a consequence the ReS_2 BL band gap is still direct in Γ and is decreased to 2.00 eV. This is clearly different for MoX_2 or WX_2 families, for which drastic changes in LCB are observed.⁵³ This observation tends to confirm the existing electronic decoupling between ReS_2 layers evidenced in experimental works^{12,17}. However for the ReSe_2 BL, it is less obvious. On the one hand, similarly to the ML case, the VB maximum is slightly shifted from Γ -point along the Γ - K_1 ($-K_4$) direction, on the other hand the CB minimum is also slightly shifted away from Γ in Γ - M_2 direction. Thus E_g is indirect with a value of 1.73 eV, when the direct gap in Γ is 1.77 eV. We have checked that the influence of the stacking order on the band-gap value is very limited, since for ReS_2 BL in AA-stacking configuration, E_g^Γ is 2.04 eV.

C. Bulk

In Figure 4 is plotted the self-energy corrected ReS_2 -bulk's band structure using high symmetry directions, as in Figure 1. Our G_0W_0 calculation predicts bulk ReS_2 to be a semiconductor with a direct fundamental band gap of 1.60 eV in Z (0,0,1/2) coordinates, when the in-plane dispersion does not change that much with a HVB-LCB separation of 1.88 eV at Γ point. Those values are in the same range of the ones reported recently in Ref.[25]. This is clearly different from others Mo and W based MX_2 families where the HVB maxima always remain at Γ and at the same time the LCB minima still lie in the (k_x, k_y) plane. For those systems relatively strong interactions between the chalcogen atoms of the neighboring layers result in the direct-to-indirect band gap crossover with increasing the number of layers, when for Re-systems the nature of band gap itself is changed, favoring

FIG. 3. On the left, the G_0W_0 band structures of ReS_2 bilayer in the most stable configuration, *i.e* with a displacement of around $2.4 \text{ \AA}$ along $\vec{a}$ of the second layer. On the right, The G_0W_0 band structures of ReSe_2 bilayer in the most stable configuration, *i.e* with a displacement of around $2.4 \text{ \AA}$ along $\vec{a}$ of the second layer. The energy level of the valence band maximum (in Γ) is set to zero.

interlayer transitions. Indeed a closer look of the orbital's character of those states clearly proves a very pronounced d_{z^2} character. The one-shot GW band structure of bulk ReSe_2 is given in Fig. 4. We observe a direct fundamental band gap of 1.38 eV at Z symmetry point. In the (k_x, k_y) plane, the top of the HVB is still located between Γ and K_4 (K_1) and the bottom of the LCB remains in the vicinity of K_3 symmetry point, retaining the in-plane band structure of the BL case mainly.

A significant band dispersion of the bands near Fermi level is observed in bulk's band structure compared with ML and BL cases for both ReS_2 and ReSe_2 . It is mainly due to interlayer interaction. Likewise, one can note a blue shift of the band-gap value upon dimensional reduction from bulk to ML as expected.

IV. ABSORBANCE

Absorbance of a single ReS_2 ML, in the D_1 structure, as a function of the frequency for the xx (Γ - M_2 direction) and yy (Γ - K_1 direction) components are given in figure 5. We recall that in ML cases for both ReX_2 systems, the VBM and CBM are doubly degenerated. This implies, as proposed by Arora *et al.*²⁵, that the first four peaks origins are the four inter-band transitions with different combinations of spin. As a consequence they are split

FIG. 4. The G_0W_0 band structures of ReS_2 bulk, on the left and for ReSe_2 bulk on the right. The energy level of the valence band maximum (in Z) is set to zero. High symmetry directions of the 1BZ in bulk crystal are depicted in Figure 1.

FIG. 5. Absorbance of monolayer ReS_2 (left) and ReSe_2 (right) in the $\Gamma\text{-M}_2$ direction (xx) and $\Gamma\text{-K}_1$ direction (yy). Vertical dashed line represents the fundamental band gap energy. The inset of the left figure presents the oscillator strengths with respect to the number of occupied and unoccupied states included in the BSE calculations.

due to exchange interaction. This is clearly shown in the inset of the left part of figure 5. As soon as the active space of the BSE calculations includes at least two occupied and two virtual states, the exchange term split excitons in two different directions. Optical anisotropy is clearly evidenced in the spectrum. Main excitonic features appear in the energy range between 1.5 and 2.4 eV. When the most stable exciton, at 1.64 eV, has contributions along xx and yy directions, the second one, that lies 0.05 eV higher in energy is mainly

oriented along Γ -M₂ (xx) direction. A similar behavior is observed for ReSe₂ ML with smaller intensities and a less pronounced anisotropic character in the first two excitonic peaks. We stress the fact that in other TMDCs this splitting does not involve anisotropy but exchange interaction and SOC⁵⁴. Interestingly in Ref.[15], they report an optical gap value of 1.61 eV for ReS₂ ML by PL and reflectance spectroscopy experiments. For ReSe₂ ML the experimental optical gap is 1.50 eV²⁵, when it is located at 1.43 eV in our calculations. The overall agreement between experimental results and our estimates is good, considering the precision of $GW+BSE$ calculations scheme.

The binding energy (BE) of the lowest exciton in ReS₂ ML is 0.74 eV, much larger than other M or W-based TMDCs. For ReSe₂ ML the BE is 0.57 eV when the exchange splitting is only 0.04 eV. The binding energy values are in line with previous reports, they only differ due to different computational details^{22,25}. Additionally, we have noticed fine structure of those peaks with the presence of a dark state 7 meV lower in energy than the bright one, and the presence of a grey exciton, possibly coupled to light with z-polarization as recently observed in WSe₂ ML⁵⁵, with a small oscillator strength 4 meV above the bright state. The next higher energy peak is seen at 1.83 eV with a stronger oscillator strength for yy component than for the xx one.

When a second layer is added to a ReS₂ ML, with two different stacking orders, there is a red-shift of the lowest excitonic peak of 0.04 eV. One can still observe the anisotropic character by decomposing the absorbance function in xx and yy directions. The orientation of the second layer with respect to the first one does not change drastically the spectrum. The only noticeable difference can be seen when the stacking is highly symmetric (AA-stacking), see Fig. 6, the peak at 1.76 eV is much more intense, due to the perfect alignment between the atomic positions. The corresponding BE is 0.40 eV for the optimized stacking order and slightly larger (0.44 eV) for AA-stacking. The screening effect on the first ReS₂ ML due to the presence of a second layer has not significant effect on the energy of the electronic transitions while the band-gap renormalization induces important changes on the BE. Despite the fact that a ReSe₂ BL has an indirect band-gap in our calculations, we have performed BSE calculations, in order to investigate direct transitions. As for ReS₂ BL, those direct transition energies are not altered by the addition of a second layer in ReSe₂. The first two direct transition are still located at 1.41 eV and 1.44 eV for the BL, a similar trend is obtained for ReS₂. Thus the electronic screening due to the second layer in ReX₂

compounds only implies a reduction of the fundamental gap, possibly altering its direct to indirect character for ReSe_2 only and reducing significantly the BE.

FIG. 6. Absorbance of ReS_2 BL in the optimized configuration (left) and in AA-stacking configuration (right) in the Γ - M_2 direction (xx) and Γ - K_1 direction (yy). Vertical dashed line represents the fundamental band gap energy.

Figure 7 shows the absorption coefficient α_2 as a function of the frequency for both bulk of ReS_2 and ReSe_2 systems. Both spectra present a rich excitonic structure in the energy range from 1.3 to 1.6 eV. By comparing in-plane contributions to the dielectric tensor, we clearly evidence the optical anisotropy still present in the bulk phase of Re-based TMDCs. In the mentioned energy range we observe that the excitonic response is slightly stronger for the yy component than for the xx one. For ReS_2 , the lowest-lying feature appears now at 1.40 eV, in good agreement with the experimental determination of the optical gap of Ref.[15], i.e. 1.47 eV. In the same article, it is reported the presence of a feature at 1.4 eV in PL but not in reflectance experiments. Based on this, they have concluded that bulk ReS_2 to be a semiconductor with indirect excitonic band gap. Marzik *et al.*⁵⁶ have concluded from their photo-electrochemical measurements an indirect band gap of 1.4 eV for ReS_2 single crystals, when from low temperature absorption measurements Friemelt *et al.*²⁸ have determined a value of 1.56 eV for the direct optical band gap of p -type ReS_2 single crystals and 1.53 eV for n -type ones. Furthermore, they have also found a sharp peak in low temperature absorption spectrum at 1.57 eV which was assigned to an excitonic peak. These values are in reasonable agreement with our findings but the assignment contrast with our conclusion, since our band structure results confirm a direct fundamental gap for ReS_2 in bulk, in Z k-

point. Concerning the optical band gap, we safely assign the feature present at 1.40 eV to be a direct excitonic band gap since in any BSE calculation only vertical transitions are taken into account. Two others intense peaks at 1.51 and 1.56 eV are theoretically determined, in very good agreement with values extracted from reflectance contrast measurements, 1.51 and 1.58 eV. The theoretical blue shift when decreasing the thickness of the sample is thus 0.24 eV, when its experimental value is 0.14 eV¹⁵. The next two main features are shifted in energy by 0.18 and 0.27 eV respectively, when experimentally those values are 0.16 and 0.30 eV. The BE of exciton in ReS₂ bulk is thus estimated to be 0.20 eV, reduced by 75% when compared to the ML limit.

FIG. 7. Optical absorption coefficient of bulk ReS₂ (left) and ReSe₂ (right) in the Γ -M₂ (xx), in the Γ -K₁ (yy) and Γ -Z (zz) directions. Vertical dashed line represents the fundamental band gap energy.

For ReSe₂ in the bulk phase, the lowest energy peak in the spectra is composed of three bright excitons, the dominant strength oscillator exciton is located at 1.16 eV and it is preceded by a couple of weaker strength oscillator excitons located few meV lower. The BE of bulk ReSe₂ is 0.22 eV considering the direct fundamental band gap also located in Z. Previous experimental works^{52,56,57} using different techniques have obtained values of 1.15, 1.17, and 1.22 eV for single crystal optical band gap respectively. More recently PL experiments⁵⁸ report a value of 1.26 eV for the optical band gap of bulk ReSe₂, when a larger value (1.37 eV) is also proposed²⁵. Globally in this case, the dispersion of the optical band gap is still relatively large. The next higher energy features are centered around 1.21 and 1.29 eV, the latter being broader for the xx component. As a consequence, the blue shift

observed on the first two peaks when reducing layer thickness from bulk to ML is 0.27 and 0.26 eV respectively. This is clearly much larger than in any others TMDCs, but probably overestimated in our calculations, when compared to experiments²⁵. The corresponding excitonic BE is 0.21 eV.

In order to study the optical anisotropy of ReX_2 compounds and, in particular, to understand the angular dependence of the low-energy features in the spectra, we have rotated the in plane dielectric tensor component on the layer around the $\vec{c}$ axis (perpendicular to $\vec{a}$ and $\vec{b}$). In figure 8, the imaginary part of the dielectric tensor of ReS_2 systems as a function of the polarization angle and the energy of the incoming light is presented. ReSe_2 results are given in Appendix D. The blue line corresponds to yy dielectric tensor component. We note that the optical anisotropy near the excitonic resonances implies that the absorption of these layers varies strongly as a function of the light polarization. For the low lying features below the fundamental gap values, the maximum is always obtained for light polarization aligned with the Re-Re chain, so with an angle of around 120° , for ML, BL and bulk too.

FIG. 8. Imaginary part of the dielectric tensor of ReS_2 systems, with respect to light polarization angle.

From bulk to ML thickness one can see an increase of the lowest excitonic peak's intensities as well as blue shift of their transition energies. For each excitonic feature in the spectra one can identify the easy polarization axis, a preferential direction where transition probability become maximum. The angle where the intensity reach a minimum corresponds to weakest oscillator strength or a polarization angle where transition are forbidden. We note that oscillator strength of the excitons in the lowest features of ML and BL has different easy

polarization direction. As a consequence, in the angular evolution of the features, those excitons seems out of phase. The variation of the intensity of the lowest energy features from xx component to yy component is an evidence of the optical anisotropy of the ReX_2 compounds. Oscillator strength of the excitonic features become stronger over dimensional reduction.

V. CONCLUSION

In the present work, we propose a theoretical study of electronic and optical properties of the layered ReX_2 compounds for ML, BL and bulk phase, by means of $GW+BSE$ scheme. For ReS_2 the band gap reminds direct, despite a change of the band-gap nature, with values increasing from 1.6, 2.0 and 2.4 eV from bulk to ML respectively. For ReSe_2 , the fundamental band gap changes from direct for bulk phase (1.38 eV) to indirect in bilayer (1.73 eV) and becomes again direct for a single layer (2.05 eV). Those results are compatible with experimental findings, and theoretical absorption spectra agree well with results from PL and reflectance experiments. Anisotropic optical properties are also evidenced and fine structure of the excitons certainly deserve further experimental works.

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Appendix A: Convergence issue of the imaginary part of the dielectric constant with respect to k-points sampling

FIG. 9. Imaginary part of the dielectric tensor of ReS₂ ML depending on k-point sampling grids.

To investigate convergence issues with respect to the k-points sampling, we have neglected SOC term but kept all the others calculation parameters as they are given in the computational details section. If one checks the first excitonic peak in the imaginary part of the dielectric constant for 3 different grids, the difference is around 0.05 eV. The position of higher energy excitons also follow the same trend, but with $12 \times 12 \times 1$ grid new features appear, probably due to a better description of excited states of the excitons. Mind that by adding SOC term, symmetry is removed in the calculation, thus increasing significantly the computational cost, that makes a $12 \times 12 \times 1$ calculation intractable in a reasonable time.

Appendix B: Binding energy of MoS₂ and ReS₂ bilayers

In figure 10, the binding energy of MoS₂ and ReS₂ bilayers in AA-stacking are given. PBE results are compared to the curves obtained by either the Tkatchenko-Scheffler method⁵⁹, the DFT-D3 method⁶⁰ or the vdW-DF2 scheme^{38,39} too. Globally similar range of energy

are obtained, meaning that ReS_2 behaves like all the others TMDCs in terms of van der Waals interactions between layers.

FIG. 10. Comparison between the binding energy of MoS₂ and ReS₂ BL for different schemes that include van der Waals forces in the hypothetical AA-stacking.

Appendix C: Stacking geometries of ReS₂ bilayers

The stability of the stacking with respect to translational displacement, along $\vec{a}$, along as well as perpendicular to $\vec{b}$ have been investigated using vdW-DF2 functional. In figure 11, the primitive cell and the lattice vectors directions are recalled, as well as the energy differences from the hypothetical AA-stacking, i.e the simplest superposition of the two layers. The atomic positions were allowed to relax too.

FIG. 11. Energy differences from AA-stacking for various distances in three directions of displacement.

Appendix D: Polarization angular dependence of the absorption spectra for ReSe₂ systems

FIG. 12. Optical absorption spectra of ReSe₂ systems, with respect to light polarization angle.

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